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Printed documents that have been considered for the judment whether a patent can be issued:

DE 1 95 07 174 A1
DE 43 44 577 A1
DE 43 27 610 A1

# Process and fixture for the production of acrylic surfaces that possess an increased abrasion and scratch resistance

A process and fixture for the production of acrylic surfaces that possess an increased abrasion and scratch resistance, characterized in such a way that one

a) utilizes a section of a mold (11, 12) that is utilized for the production of an acrylic sheet
b) initially applies a gel coat (12)
c) that contains in a determined concentration nano scaled particles with a dimension between 10 and 100 nm
d) that are distributed in a homogeneous fashion in the gel coat
e) subsequently fills into this mold the still liquid pre-polymer to be used for the production of the acrylic sheets
f) and that, following this process, will be allowed to cure
g) and one thus, following the curing process, obtains an acrylic sheet that was created with said pre-polymer
h) that possesses a coating which was created from the gel coat layer.

## Description

The presented invention is concerned with a process and fixture for the production of acrylic surfaces that possess an increased abrasion and scratch resistance. Acrylic surfaces of this kind are desired, for example, for sanitary objects such as bathtubs or shower tubs.

Known from the state of the art of this technology are processes for the production of sanitary equipment made of plastic materials based on polymethyl methacrylics. For example, described in the DE 43 44 577 (A1) is such a process. Also known from this document is to add particle shaped inorganic filling substances to the polymethyl methacrylics (PMMA). Herewith, such filler particles are of a relatively small dimension, however, the particle size ranges around 20 to 60 µm. With this known process however, the sanitary objects are produced by means of a resin casting process, with which the entire resin suspension contains the mentioned filler substances. This results in the case that the filler substances are distributed across the entire volume of the finished PMMA sheet. With this known process, the filler substances are also utilized for the purpose of increasing the thermal durability of such sanitary objects produced with such plastic material.

Another process of the state of the art of the technology that is described in the DE PD 43 13 715 (A1), also explains the production of polymer materials that are based on PMMA while utilizing inorganic, particle shaped filler substances that possess a particle size that preferably lays in the range above 10 µm. However, foamed PMMA materials are produced with this process. These materials are not well suited for the production of sanitary objects that are to have specifically abrasion and scratch resistant surfaces.

Known from the DE 43 27 610 (A1) are cast PMMA sheets that are produced in a polymerization chamber by means of polymerization and that contain a particle shaped filling substance. Initiators are added for the polymerization, and subsequently the mass solidifies inside the chamber. However, the utilized individual particles are relatively large with their particle size of 0.5 to 60 µm. This situation leads specifically to the condition that the surface possesses a roughness that one can feel and probably even see. Furthermore, it is not always desired that the particles are evenly distributed in the entire mass. This however, is the case with the sheets that are produced following the DE 43 27 610 (A1).

Subject of the DE 195 07 174 A1 is the scratch resistant coating of plastic materials that are based on PMMA. Herewith, coating substances are applied onto shaped bodies that consist of pre-polymer and monomer compositions that are mainly monomers, respectively, pre-polymers based on acrylates or methacrylates. For example, polymer methacrylate plastic sheets will be coated. However, according to the DE 195 07 174 A1, herewith one will try to achieve the desired scratch resistance with support of the specific composition of the purely organic coating substance. The utilization of filler substances is not mentioned here. Furthermore, an already finished (plastic material) shaped body is already present with the DE 195 07 174 A1. Said shaped bodies will be subsequently coated in separate processing steps. This, of course, will lead to a much increased processing involvement and related higher production costs.

The scope of the presented invention is to provide a process, respectively, a fixture for the production of acrylic surfaces that possesses an increased abrasion and scratch resistance, and with which acrylic sheets will be obtained that can be deep drawn, and that are thus suitable for the manufacturing of sanitary objects such as, for example, of bathtubs or shower tubs that are produced in a subsequent deep drawing process.

The solution for solving this scope is delivered by a process according to the kind mentioned in the beginning that has the identification characteristics of the main claim. A fixture that is suited for execution of this process is described in claim 13.

With the process that is executed according to the invention, one initially produces a so called gel coat that consists of a reaction resin based on methyl methacrylate that contains a certain concentration of ceramic and other inorganic particles with a dimension that ranges in the nano-scale (for example, 20 volume %) that are distributed in a homogeneous fashion in the reaction resin.

Said gel coat is a high viscous mixture, and prior to the processing, it will be mixed with a hardener, for example, with benzoylperoxide. With the process that is executed according to the invention, said gel coat is practically applied onto the mold, for example, a lower glass plate, prior to the execution of the actual acrylic sheet production.

There are a variety of application possibilities for said gel coat. It is preferred that one utilizes spraying, rolling, or raking processes as the application method.

The production of the acrylic sheets occurs by means of casting the substance in between two glass sheets that are utilized as a mold, and with which the mass will cure subsequently. Herewith, one applies said gel coat onto one of the glass sheets that is utilized as part of the mold, allows it to form a gel thereon (curing, partially cross linking) and subsequently, one fills the liquid MMA (pre-polymer) into said mold. This will initiate the polymerization process, and the material cures and becomes solid. With other words, as a result of the production process one immediately obtains an acrylic sheet that is coated with an abrasion resistant layer, which is comprised of particles in a nano-scaled dimension range.

The liquid MMA for the acrylic sheets (which thus means for the sheet body that is to be coated), preferably consists, prior to the polymerization process, of a mixture consisting of monomers, pre-polymers, pigments, and other additives.

In order to be able to determine the material thickness of the entire sheet, one preferably utilizes a PVC cord that is inserted in between the two glass sheets that create the mold, and with which said PVC cord is placed around the entire circumference of said glass sheets, which thus determines the desired relevant thickness of the material.

The two glass sheets that are utilized as being the mold are preferably held together with each other and the cord by means of wire clips.

Prior to positioning the cord onto the, preferably, lower glass sheet, and prior to the process of connecting said cord and the lower sheet with the upper glass sheets by means of said wire clips, the gel coat for the coating should at least be partially cross linked (to ensure that it has an adequate viscosity). Thus, for this case, the gel coat will be applied to the lower glass sheet, and the upper glass sheet will subsequently be placed onto the system.

An alternative to this process would be that one initially casts the acrylic sheet without the coating, and that one subsequently applies the gel coat layer by means of spraying, rolling, or raking processes once said acrylic sheet was removed from the mold. However, this alternative requires that the coating is self-leveling and that the curing will occur rather rapidly. It is of advantage that one executes the polymerization in such a manner that ensures that the produced plate is free of monomers.

It is preferred that the thickness of the layer that is produced by the gel coat shall be in the range of ≥ 0.4 millimeters. The coating results in an increased abrasion resistance, and also in an increased scratch resistance of the treated surface.

The concentration range of the nano-scaled particles ranges, preferably, between 2 and 30 %, even more preferably it is in the range between 5 and 20 %.

In principle, the nano-scaled particles can consist of any desirable crystalline nano-scaled particles. Herewith, it is preferred that the nano-scaled crystalline particles consist of inorganic particles, for example, of oxides, for example, considered for this can be $TiO_2$, $SiO_2$ ,$Al_2O_2$, or similar substances.

The dimension of the nano-scaled particles lies, preferably, mostly in the range of 10 and 100 nm, even more preferred, it lies in the range in which most of the particles have a dimension of 60 and 80 nm. Thus, the particle dimension of the nano-scaled particles is much smaller than this is the case with the inorganic filler materials that are used in the above-mentioned processes that are executed according the state of the art of the technology.

The gel coat that is utilized in the process that is executed according to the invention can contain, for example, a reaction resin that is based on methyl methacrylate that preferably contains up to 30 % of nano-scaled particles that are dispersed in said resin. Furthermore, it is possible that the gel coat can contain a curing enhancer, for example, in an amount of 0.1 to 5%, and preferably in an amount that ranges between 0.5 and 1.5 %. Furthermore, it is preferred that the gel coat contains a peroxide in an amount that ranges, for example, between 1 and 5 %, and preferably in an amount around 3 %. Preferably suitable as enhancers are, for example, amines, for example, a preferred utilized enhancer is dimethylamine. Suitable as a peroxide is, for example, dibenzoyl peroxide.

The thickness of the applied gel coat layer onto the glass sheet of the mold will be, preferably in a thickness of 0.2 to 2 mm, and even more preferable the application thickness should range around 0.4 mm to 1 mm. Following an alternative execution process of the invention, it is also possible that the application of the gel coat can also occur after the removal of the acrylic sheet from the mold.

The characteristics that are stated in the sub claims are concerned with preferred further execution examples of the process that is executed according to the invention.

Further advantages of the invention will result from the following detailed description.

In the following, the presented invention will be described in more detail with the support of an execution example and in reference to the attached drawings. Displayed herewith is in:

Fig. 1 a fixture for the production of an acrylic sheet according to the invention, as well as the thus produced acrylic sheet during the production process;

Fig. 2 a finished acrylic sheet after the production process.

As it can be seen from Fig. 1, the fixture that is made according to the invention comprises an upper glass sheet 10 and a lower glass sheet 11. A gel coat 12 that contains the nano-scaled particles, and that is to later create the abrasion resistant surface of the acrylic sheet was applied onto the glass sheet 11. Preferably, the thickness of the applied gel coat 12 ranges between 0.4 millimeter and 2 millimeter.

Furthermore, the fixture is equipped with a surrounding sealing cord 13 that is located in between the upper glass sheet 10 and the lower glass sheet 11. Said sealing cord 13 is supposed to prevent the filled in pre-polymer 14 from escaping out of the mold. With other words, the two glass sheets 10, 11 practically create the mold for the production of the acrylic sheet. The pre-polymer 14 can be filled in on top of the gel coat layer 12 that is applied to the lower glass sheet 11. Subsequently, the upper glass sheet 10 can be placed on top of the lower glass sheet. Herewith, it is preferred that the two glass sheets 10, 11 of the fixture are held together with the support of wire clips 15, 16 that are arranged, for example, in the same distances from each other around the circumference of the fixture. At this point, the pre-polymer will be filled in between the two glass sheets, on top of the gel coat layer that was applied to the lower glass sheet, with the support of a "filling wedge". Subsequently, one will obtain an acrylic sheet that possesses a defined thickness with an abrasion and scratch resistant top surface after the polymer mixture is cured. Herewith, said scratch and abrasion resistant top surface also possesses a defined layer thickness that is created by the cured gel coat 12. The nano-scaled particles are present only in this top surface layer.

Fig. 2 displays a finished acrylic sheet 17 after removing it from the mold. As one can observe, said sheet consists of a lower layer, which means a carrier layer consisting of acrylic glass that is identified with 18 that correlates with the above mentioned layer identified with 14, which consist of the pre-polymers. The thin upper surface layer 19 of the acrylic sheet 17 has been created from the above mentioned gel coat layer 12. The two layers 18, 19 of the acrylic sheet 17 are connected solidly and in a durable manner with each other, and they allow for a subsequent deep drawing process required for the production of a sanitary object of any desired shape. Herewith, the surface does not display any cracks or material splintering.

**Patent Claims**

1. A process and fixture for the production of acrylic surfaces that possess an increased abrasion and scratch resistance, characterized in such a way that one
   a) utilizes a section of a mold (11, 12) that is utilized for the production of an acrylic sheet
   b) initially applies a gel coat (12)
   c) that contains in a determined concentration nano scaled particles with a dimension of between 10 and 100 nm
   d) that are distributed in a homogeneous fashion in the gel coat
   e) subsequently fills into this mold the still liquid pre-polymer to be used for the production of the acrylic sheets
   f) and that, following this process, will be allowed to cure
   g) and one thus, following the curing process, obtains an acrylic sheet that was created with said pre-polymer
   h) that possesses a coating which was created from the gel coat layer.

2. A process for the production of acrylic surfaces according to claim 1, characterized in such a way that the gel coat contains a reaction resin that is based on methyl methacrylate.

3. A process for the production of acrylic surfaces according to claim 1 or 2, characterized in such a way that a hardener was added to the gel coat prior to the processing of the same.

4. A process for the production of acrylic surfaces according to the claims 1 through 3, characterized in such a way that the gel coat contains the nano-scaled particles in a concentration between 2 and 30 %, preferably in a concentration between 5 and 20 %.

5. A process for the production of acrylic surfaces according to the claims 1 through 4, characterized in such a way that the gel coat contains inorganic nano-scaled particles that are of a crystalline structure.

6. A process for the production of acrylic surfaces according to the claims 1 through 5, characterized in such a way that the gel coat contains crystalline nano-scaled particles that consist of an inorganic oxide, preferably of $TiO_2$, $SiO_2$, or $Al_2O_2$.

7. A process for the production of acrylic surfaces according to the claims 1 through 6, characterized in such a way that the dimensions of the nano-scaled particles in the gel coat lay in the range between 60 and 80 nm.

8. A process for the production of acrylic surfaces according to the claims 1 through 7, characterized in such a way that the gel coat consists of a reaction resin that is based on methyl methacrylate that contains up to 30 % of the nano-crystalline particles in a dispersed condition, and that it also contains a curing enhancer in an amount between 0.1 to 5 %, preferably in an amount of 0.5 to 1.5 %, as well as a peroxide in an amount between 1 to 5 %, preferably between 2 and 4 %.

9. A process for the production of acrylic surfaces according to the claims 1 through 8, characterized in such a way that the gel coat is applied in a thickness between 0.2 and 2 mm, preferably between 0.4 and 1 mm.

10. A process for the production of acrylic surfaces according to the claims 1 through 9, characterized in such a way that the gel coat is applied by means of spraying processes, or that the application occurs by means of rolling, raking or similar processes.

11. A process for the production of acrylic surfaces according to the claims 1 through 10, characterized in such a way that two glass sheets (11, 12) are utilized as the mold for the production of the acrylic sheet, and that the gel coat (12) will be applied onto one of those glass sheets in the form of a coating prior to filling the pre-polymer (14) into said mold.

12. A process for the production of acrylic surfaces according to the claims 1 through 11, characterized in such a way that the gel coat is applied to the lower (11) of the two glass sheets that comprise the mold.

13. A fixture for the production of acrylic sheets that possess a surface that displays an increased abrasion and scratch resistance, characterized in such a way that the fixture is comprised of an upper glass sheet (10) and a lower glass sheet (11) that together create the mold for the production of the acrylic sheet, and that are held in a predetermined distance to each other, and with which a sealing cord (13) that surrounds the circumference of said glass sheets (10, 11) is projected to be present in between those two glass sheets (10, 11), and with which the said two glass sheets (10, 11) are held together with the support of clamps (15, 16) that are located around the entire circumference of said glass sheets (10, 11).

14. An acrylic sheet that possesses a top surface with an increased abrasion and scratch resistance, characterized in such a way that the same is produced following a process with the characteristics of one of the claims 1 through 12.

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Herewith 2 sheets of drawings

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